

## ON MOSAIC CRYSTALS

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A. *Statement of the Problem.*—Very little progress has been made during the last decade toward a theoretical understanding of the physical properties of matter in the solid state. The reasons for this stagnation are very clearly presented in a recent paper by A. Smekal.<sup>1</sup> According to Smekal, the properties of solids can be arranged in two large groups as follows.

Properties of the first type are "structure insensitive." For a given substance, they are practically the same (no change in order of magnitude) whether we deal with single crystals or polycrystalline agglomerates. Examples are the density, the energy content, the thermal coefficient of expansion, the lattice structure as determined by x-rays, etc.

Properties of the second type are "structure sensitive," since they may be altered considerably by plastic deformation, by changing the size of the grain or by introducing small amounts of contaminations. They include the elastic limit, the breaking strength, the thermal and the electrical conductivity, etc.

Now it is well known that the theory of ideal lattices as developed by Laue, Bragg, Kossel, Born and others satisfactorily takes account of structure insensitive properties. Unfortunately, this theory is utterly helpless in regard to the structure sensitive properties. For instance, the values which have been deduced theoretically for the mechanical and the electrical strength are about 100 to 1000 times too large. But still more serious is the fact that the general phenomenon of plasticity of single crystals cannot be interpreted in any way on the scheme of ideal lattices. Such a lattice would indeed be perfectly elastic for any load not causing actual rupture.

Following A. Smekal, we may say that the central problem of the physics of crystals is to find a rational answer to the question, "How can we understand the coexistence of properties of the two groups mentioned above, making use only of the fundamental properties of the molecular building stones?"

In the following, I am sketching the main outlines of a theory which I think will provide the solution of the problem stated above. The most important feature will be, that ideal crystals, though dynamically stable, are thermodynamically unstable. *The thermodynamically stable forms are not completely characterized by the lattice structure as it is deduced from the x-ray structure analysis. On top of this primary structure, there is*

*superposed a secondary structure, which shows perfect regularity also. In general it has to be interpreted as a slight periodic variation in density. The elementary spacing of this secondary structure will for most of the crystals be found in the region between 100 and 10,000 Å.*

The solution proposed here for our problem is that all the properties of the first type are determined by the primary lattice, whereas the structure sensitive properties are mainly related to the secondary structure.

B. *Stability of Lattices—Mosaic Crystals.*—Let us define at first an ideal crystal. Such a crystal does not exist, but it will be a convenient starting point for our considerations. An ideal crystal satisfies the following two conditions.

1. Geometrically, it is described completely by one of the mathematically possible crystallographic groups. The elementary space of the lattice corresponds to that which is obtained by the x-ray structure analysis.

2. The total energy  $E$  of the crystal shall be a minimum against all infinitesimal variations of the lattice which transform this into a configuration satisfying again condition (1).

It must be mentioned that the possible variations of the type (2) do not represent independent conditions. Consider, for instance, a regular crystal which is built up by particles exerting forces on each other which are functions of the distance only. If for such a crystal  $E$  is a minimum, against a uniform compression it will be a minimum against every other variation of the type (1), shearing for instance.

Two important questions now arise. The first is whether the ideal crystal is really dynamically stable. In other words, is the energy a minimum relative to all small variations of the lattice, regardless of whether they are of the type (2) or not? In the second place, we want to know if the ideal crystal is also thermodynamically stable. The answer to this question will give us the sought-for information about the constitution of actual crystals. On it we concentrate our main interest. The first question also deserves much attention for reasons which will be mentioned later.

From the fundamental laws of thermodynamics, it follows that the thermodynamically stable configuration of an assembly of particles is characterized by the fact that its free energy is an absolute minimum. If we disregard the thermal agitation for the moment, the condition is that the total energy is an absolute minimum. Our results then will be correct in the neighborhood of the absolute zero point.

It must be understood that we are not interested for the present as to which different types of modifications of crystals may be obtained from given atoms, diamond and graphite, for instance, if we deal with carbon atoms. We are rather looking for finite, although not too large variations, which, when exerted on an ideal lattice will decrease its energy, the final

configuration, however, not being represented exactly by any crystallographic group, but only approximately so. I have pointed out one such variation in an earlier paper<sup>2</sup>) a variation which is equivalent to the formation of cracks. I have tried to extend the considerations given there, and I have found that the opening of cracks is not really the most fundamental effect in relation to our problem—I rather think, now, that it is secondarily related to a simpler phenomenon, namely, the secondary structure of crystals which was mentioned above.

I can indicate here only the general outlines of the reasoning which led me to the above conclusions. A complete quantitative discussion will be published in another place.

From the general phenomenon that a lateral contraction results when a crystal is extended, we conclude that a single lattice plane, if it were not sandwiched between other lattice planes would be characterized in the equilibrium state by a smaller spacing than the three dimensional lattice. Let us discuss the simplest case of a cubical crystal whose lattice constant is  $d_0$ . A single plane in equilibrium, then, is characterized by a spacing  $d < d_0$ . For NaCl, it can be deduced theoretically that  $d = 0.94 d_0$ . In order to have an isolated plane with the spacing  $d_0$ , a certain uniform tension has to be applied, which may be, say,  $X$  dynes/cm. This suggests choosing as a variation of the ideal lattice a relative linear contraction  $\delta$  of just one plane, say, II. If we consider only the forces exerted by particles belonging to this plane, the work done would be

$$dW_1 = -2SX\delta \quad (S = \text{surface}). \quad (1)$$

Considering now the forces acting between II and the rest of the planes, it is evident that they will resist a contraction of II. If we calculate the work which we have to do to produce a contraction, we obtain in the first approximation

$$dW_2 = \kappa\delta^2 \quad (2)$$

where  $\kappa > 0$ . It can be seen very easily that there will be no term proportional to  $\delta$ . From this we conclude that the total change of energy

$$dW = dW_1 + dW_2 < 0$$

for a very small  $\delta$ . It is clear that  $\delta$  must be very small indeed; otherwise, such atoms of II which are very far apart would change their mutual distance by amounts larger than  $d_0$ , in which case, the relation (2) could not be written down directly. The argument can, however, easily be made rigorous by considering the following finite change of configuration.  $\alpha$ ) Contract II so that its spacing is changed from  $d_0$  to  $d$ .  $\beta$ ) Fill the gaps which have been opened by  $\alpha$ ) between the two parts of the crystal I and II, which are separated by II.  $\gamma$ ) Rearrange the relative position

of I and II in a certain way. Then, if the total energy change for  $\alpha$ ),  $\beta$ ),  $\gamma$ ) is computed one finds, in general, that it is negative. Thus, the contraction of one definite plane of the crystal will lead to a thermodynamically favored state. Now this process can be repeated for a plane  $\Pi_1$  which is far enough away from  $\Pi$  that the effect of the contraction of  $\Pi$  is not noticeable; then for a plane  $\Pi_2$  and so on. The greatest gain

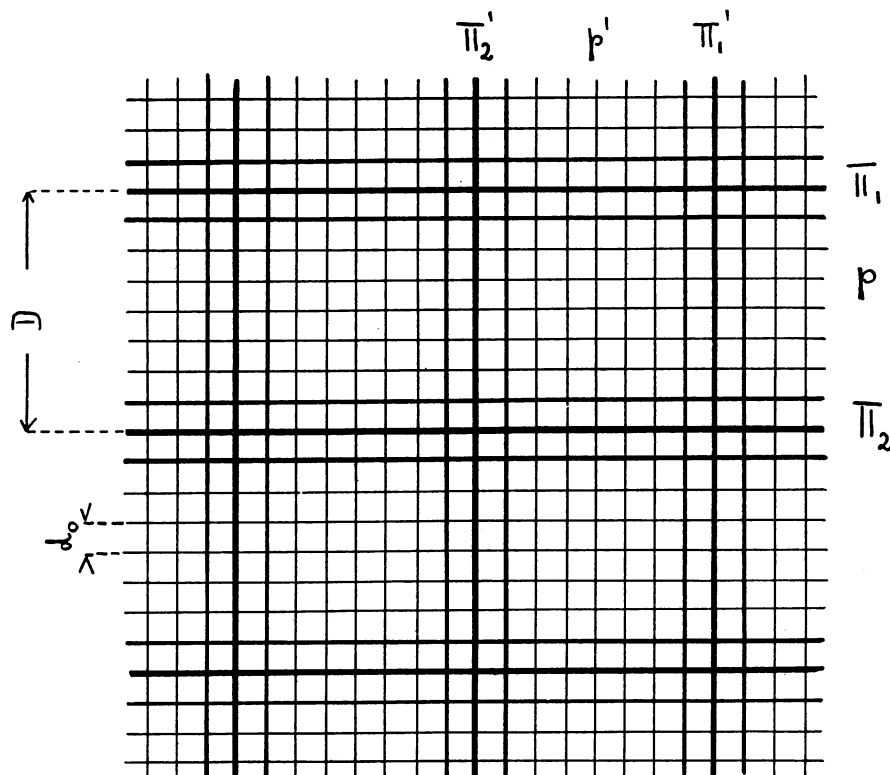


FIGURE 1

in energy will be obtained if, for the distance  $D$  between the planes, the smallest possible one is chosen. This means that the thermodynamically stable state will be characterized by constant spacings  $D$ . For our regular crystal, the argument can be extended to all three directions which leads to the conception of a secondary structure of the crystal, defined by a periodic change in density with the period  $D$ . A plane section is schematically shown in figure 1. The width of the lines represents line density. Our argument is based on the existence of a lateral contraction on extension. A secondary structure as described in the above should therefore be found in the great majority of crystals. As to the numerical value of  $D$ , the theory leaves open an approximate range from  $D = 100 \text{ \AA}$  to  $D =$

10,000 Å, the tendency being for heteropolar crystals to favor the lower end of the scale, whereas homopolar substances will have large spacings. In regard to the space groups characterizing the primary and the secondary structure, it must be remarked that they are not necessarily the same, as will be elaborated in another place.

C. *On Optical Verifications of the Theory.*—It should be possible to test our theory by optical means in four ways.

(1) The pattern  $\Pi_i$ ,  $\Pi'_i$  can be used as a surface grating. If  $D$  is in the visible range, it must be possible to observe the crossed grating in the microscope, directly.

(2) The phenomena which Bragg and Laue discovered for hard x-rays should have their analogue for longer wave-lengths (soft x-rays to visible light) if use is made of the secondary crystal structure.

(3) As the chemical energy of atoms along  $\Pi$  and  $p$  planes is different, the speed of etching or of evaporation must also be different. In many cases, the resulting "fine structure" of the etching figures on single crystals will be observable in the microscope.

(4) Ghosts should be expected for the usual x-ray lines obtained by the Bragg method.

A systematic search was immediately undertaken in order to test the above predictions made by the theory. The following very interesting results have been arrived at so far.

a. Dr. A. Goetz, Mr. M. Hasler and myself discovered on a perfect (111) plane of Bi, three sets of parallel lines making angles of  $60^\circ$ . Dr. A. Goetz who had grown the Bi single crystals then investigated the phenomenon very thoroughly, correlating it with the etching effect (3) which he also discovered. He will publish his results shortly. I mention only that the pattern is of perfect regularity and corresponds to  $D = 1.2\mu$ .

b. My attention then was called to certain phenomena discovered by Stokes and described by R. W. Wood.<sup>3</sup> Potassium chlorate crystals often show what might be called "Bragg reflection" in the visible region. The crystals are perfectly transparent. If white light falls on the crystal at a definite angle, the reflected light is of a spectral color which depends on the angle of incidence. This and several similar phenomena I am inclined to interpret as Bragg reflection due to the secondary structure of the crystal.

c. Dr. Goetz found that single crystals of zinc after being etched produce a spectrum on illumination with white light. The effect can be observed in three positions due to the hexagonal structure of the crystal. A more complete investigation is under way.

d. Finally, I was able to identify effect (3) for Cu. Etching pictures of Cu single crystals have been published by the metallographic Laboratory of the Brown Boveri Co.<sup>4</sup> Equidistant steps in the etching grooves can very clearly be distinguished. The spacing is approximately  $D = 2\mu$ .

D. *Mechanical Properties of Single Crystals.*—The great ease with which slipping can be produced in many crystals has been a puzzle for a good many years. For rocksalt, for instance, the theory of ideal heteropolar crystals predicts a minimum load of about 10,000 kg./cm.<sup>2</sup> which would cause slipping. The observed critical load, however, is only about 20 kg./cm.<sup>2</sup> On our theory, the solution of the paradox is obtained at once. The planes  $\Pi_i$ ,  $\Pi'_i$  which might be termed as being "out of phase" facilitate the process of slipping immensely. To quantitatively determine the critical shearing strength along a  $\Pi$  plane for NaCl presents no difficulties, and agreement with the observations is obtained. It might be mentioned here that the formation of cracks which I have treated in an earlier paper<sup>2</sup> has probably to be considered as a secondary phenomenon, occurring preferentially along  $\Pi$  planes.

Slipping usually results in a permanent deformation as the elementary blocks all along the slip planes will be turned irregularly. This provides immediately an explanation for the so far obscure plasticity of single crystals.

One very important feature of the theory is that it accounts readily for the hysteresis properties of single crystals. Our secondary structure  $\Pi_i$ ,  $\Pi'_i$  will indeed change its dimensions with the temperature  $T$ .  $D$  will, in general, decrease if  $T$  is increased. But, actually, the transition from one equilibrium pattern to another will only take place if  $T > T_i$  ( $T_i$  = ignition temperature). This follows from the fact that all the different patterns represent dynamically stable configurations. A certain thermal energy is, therefore, needed to cause the transition to the thermo-dynamically stable position. Dr. H. M. Evjen of this Institute has quantitatively discussed those questions related to the velocity of reaction for the case of rocksalt. His results will be published in the *Physical Review*.

Schematically, we can represent the dependency of a definite structure sensitive property  $P$  on  $T$  as shown in diagram 2.  $P$  is a univalued function of  $T$  for  $T > T_i$ . In the region  $T < T_i$ ,  $P$  may assume any value from a certain  $P_0$  to  $P_i$ . The rectangular region, therefore, might be called the field of hysteresis phenomena. For NaCl, for instance, observations show that crystals obtained from the melt and crystals grown out of solution show different properties when investigated at room temperature, as should be expected from the theory. The observations also check the conclusion that  $D$  decreases with increasing  $T$ .

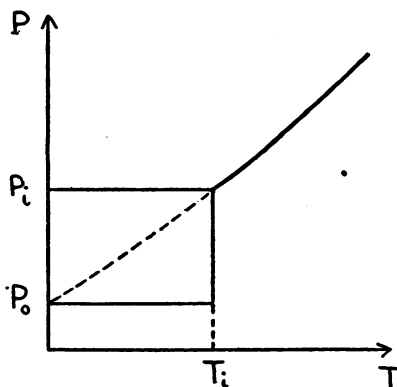


FIGURE 2

E. *Chemical and Electrical Phenomena*.—I have mentioned already that the average chemical energies along the  $p$ - and the  $\Pi$  planes are different. This has an important bearing on chemical surface reactions, on electrode potentials, etc.

As A. Smekal has shown, the electrical conductivity of insulators is mainly determined by the imperfections of the crystal structure. The occurrence of imperfections, on the other hand, is essentially related to the secondary structure of the crystals which shows that the proposed theory promises a new view on a great number of interesting phenomena. A detailed account of the theory of mosaic crystals will be published in another place. The purpose of this paper is to outline the main features of the problem and its tentative solution.

<sup>1</sup> A. Smekal, *Zeits. Phys.*, **55**, 289, 1929.

<sup>2</sup> F. Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 253, 1929.

<sup>3</sup> R. W. Wood, *Phys. Opt.*, 160, 1911.

<sup>4</sup> *The Brown Boveri Review*, January, 1929.

## ON THE FOUNDATIONS OF RELATIVISTIC COSMOLOGY

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The general theory of relativity attributes the particular metrical properties of the space-time universe, considered as a 4-dimensional Riemannian manifold, directly to the distribution of matter within it, and has naturally led to speculations concerning the structure of the universe as a whole, in which the local irregularities caused by the agglomeration of matter into stars and stellar systems are disregarded. Chief among the resulting relativistic cosmologies are those based on the cylindrical world of Einstein<sup>1</sup> and the spherical world of de Sitter;<sup>2</sup> the line elements on which these interpretations are based have not, however, been derived from the intrinsic properties of homogeneity and isotropy attributable *a priori* to such an idealized universe, but rather are presented as defining manifolds which do possess the desired uniformity. It is the purpose of the present note to formulate explicitly an assumption embodying the uniformity demanded by such a cosmology and to deduce all line elements satisfying it.<sup>3</sup> We shall find that the only possible *stationary* cosmologies—i.e., the intrinsic properties of which are independent of time—are in fact those of Einstein and de Sitter, and that they arise from particular cases of a class of solutions whose general member defines a non-stationary cosmology.

We first introduce coördinates  $x_\alpha$  (Greek indices = 0, 1, 2, 3; we write  $x^0 = t$ ) in which the line element assumes the form